REVIEW OF RESEARCH
ISSN: 2249-894X
IMPACT FACTOR : 5.7631(UIF)
UGC APPROVED JOURNAL NO. 48514
VOLUME - 8 | ISSUE - 9 | JUNE - 2019

COPPER(II) COMPLEXES WITH ASPARTIC ACID AND GLUTAMIC ACID

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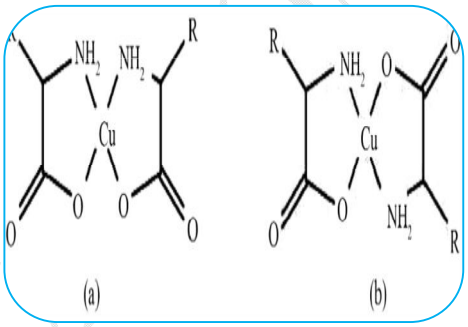
ABSTRACT:

This paper reports the dissimilar complexes of Copper(II) with different amino acids, specially aspartic acid and glutamic acid.It is generally accepted that aspartic or glutamic acid act as tridentate bridging ligands to the metal ions in an extended chain configuration by theloss of both acid protons, giving rise to polymeric complexes. But there are two examples of glutamic acid where itacts as bidentate chelating mono-negative ligand where oneof the carboxylate groups is deprotonated and coordinated tothe metal while the other remains protonated.



KEYWORDS: *Cu(II) complexes; Aspartic acids; Glutamic acid;Tridentate bridging ligand; Polynuclear, chelate, Bidentate mono-negative ligand.*

INTRODUCTION

Polynuclear copper(II) systems have received the attention of coordination chemists as they are ideal systems for developing new functional molecule based materials, for understanding the fundamental science of magnetic interactions and magnetostructural correlations in molecular species, and for their use in catalysis. Moreover copper(II) compounds are widely found in nature and are present in many oxidase enzymes (e.g. ascorbate oxidase, lactase and ceruloplasmin)[1] as an oxygen carrier in invertebrates and in photosynthesis. Although increasing attention has been paid to the design of copper complexes with polydentate ligands as model of copper oxidases, the use of multinuclear copper complexes for such reactions still remains a challenge for the synthetic chemists. On the other hand, dinuclear, trinuclear and polynuclear copper(II) complexes have received great attention in the studies of exchange-coupling interactions between adjacent metal centers.[2] So designing of copper complexes with polydentate organic ligands, with at least two donor atoms, mostly N, O donors is an active area of current research in inorganic and bio-inorganic chemistry. A very good example of N,O donor ligands are various types of amino acids. The α-Amino acids as protein constituents are small molecules withvarious functional groups. They are excellent metal complexing agents forming chelates through the amino and carboxylato groups.[3] In addition they often have a side chain with a metal binding group, such as the imidazole group of histidine (his), the side chain carboxylato group of aspartate (asp) and glutamate (glu), and the phenol ring of tyrosine (tyr), which serve as the metal binding sites in proteins.[3,4] Copper complexes of amino acids are of continuous interest, since they are model systems to study metal-protein interaction and alsoamino acid complexes of copper(II) are well knownto be important for metal ion transport in blood.

The copper(II) complexes of L-aspartic acid or L-glutamic acid have received considerable attention because of interest in their biological and coordinative properties since such ternary complex contains a hetero-atomic N base moiety and O donors in the coordinative sphere of copper(II) ion which is a preferred combination of donor atoms present in many naturally occurring mixed-ligand complexes of low and high molecular weight as it enhances the complex stability. In particular the presence of biologically important amino acid in the polynuclear ternary complexes makes the complex a realistic mimic for copper enzyme or copper-nonenzymatic proteins, especially for those containing non- or low-blue copper(II) atoms.

Copper–glutamate and copper-aspartate complexes and their adducts with amines have been extensively investigated in both solution and solid state because in metalloproteins, carboxylate ligands provided by side amino acid chains are of biological relevance in various systems such as the proton pump,[5] cytochrome bo$_3$[6] etc. It is generally accepted that glutamic acid or aspartic acid acts as a bridging ligand to two or three metal ions in an extended chain configuration by the loss of both acid protons, giving rise to polymeric complexes.

One-dimensional polymer like –Cu–asp–Cu–asp–Cu–1Dchains is observed in diaqua(L-aspartato)copper(II) complex.[7] The Cu^{II}ion is in a square-pyramidal coordination with an aspartate ion acting as a bidentate ligand through the amino nitrogen and one α-carboxylate oxygen atom, a β-carboxylate oxygen of another aspartate ion and a water oxygen, all at the pyramidal base (Figure 1). Second water oxygen is at the pyramid apex. Magnetic susceptibility data obtained between 5 K and room temperature show an antiferromagnetic behavior, with a peak value at about 7 K, and no indication of a phase transition to a 3D ordered magnetic phase.

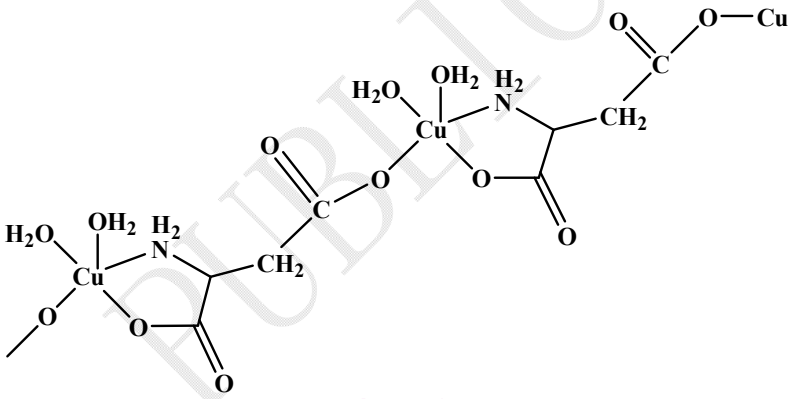


Figure 1

The *syn-anti* bridging mode of aspartic acid have been employed to construct a 2D polymeric network in [(L-aspartato)(imidazole)copper(II)dihydrate], in which each copper atom is coordinated in a distorted square-pyramidal geometry by three aspartate ions and one imidazole molecule (Figure 2).[8] In this complex each metal binds three aspartate ions at a time i.e. one copper(II) ion is coordinated with *β*-carboxylate oxygen of two aspartate ions and one amino nitrogen and *α*-carboxylate oxygen atom of another aspartate ion.

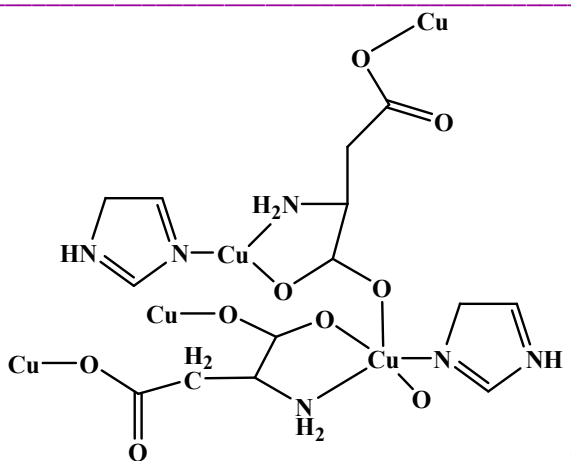


Figure 2

A mononuclear copper(II)-aspartate aqua(L-aspartato)(2,2'-bipyridine)copper(II) trihydrate complex has been reported with chelating 2,2'-bipyridine ligand.[9] The geometry around $Cu^{II}$is five-coordinated distorted square-pyramidal. The aspartate anion and bipyridine act as bidentate cheating ligand in the basal plane, with a water molecule occupying the apical position (Figure 3).

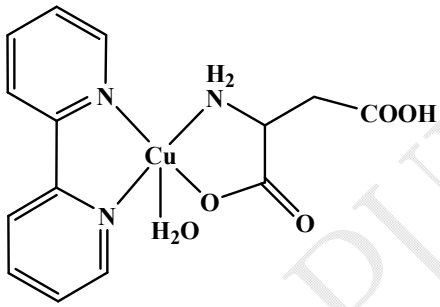


Figure 3

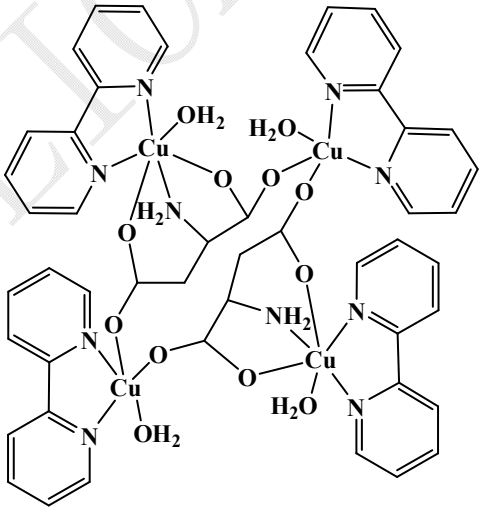


Figure 4

A new tetrameric Cu^{II}cluster with square topology exhibiting ferro- andantiferromagnetic magnetic exchange path-way has been synthesized by utilizing the *syn-anti* bridging mode of aspartic acid (Figure 4).[10] There are two independent copper atoms Cu(1) and Cu(2) have different environments with square planar geometry. The global magnetic coupling is ferromagnetic but theoretical DFT/B3LYP calculations have been carried out to assign which Cu–aspartate–Cu side is ferro or antiferromagnetically coupled.

Different coordination behavior of L-glutamic acid have been used for synthesizing three ternary complexes of formulas $[Cu(L\text{-}glu)(im)]_n$, $[Cu(L\text{-}glu)(bpy)]_n$ and $[Cu(L\text{-}glu)(o\text{-}phen)]\cdot 4H_2O$ (L-glu = L-glutamate anion, im = imidazole, bpy = 2,2'-bipyridine and o-phen = o-phenanthroline).[11] The Cu(L-glu)(im) complex has a one dimensional polymeric structure, due to square-planar metal bridging by the glutamate ligand acting as a bidentate ligand through its α-glycinate portion and bonding to a

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second metal atom through the side-chain carboxylate. The same polymeric structure and the same metal binding by the glutamate ion occur in the Cu(L-glu)(bpy) complex but in a square-pyramidal geometry(Figure 5). The structure of $[Cu(Lglu)(o\text{-}phen)H_2O]\cdot 4H_2O$ is made up of discrete mononuclear units, in which the glutamate ion acts as a simple bidentate ligand toward a s uare pyramidal Cu atom. Yang *etal,*[12] have also reported a mononuclear complex $[CuCl(L\text{-}glu)(phen)]\cdot H_2O$ with 1,10-phenantroline,in which the glutamate ion acts as a simple bidentate ligand toward a square-pyramidal copper atom and chloride anion coordinated to the axial position .

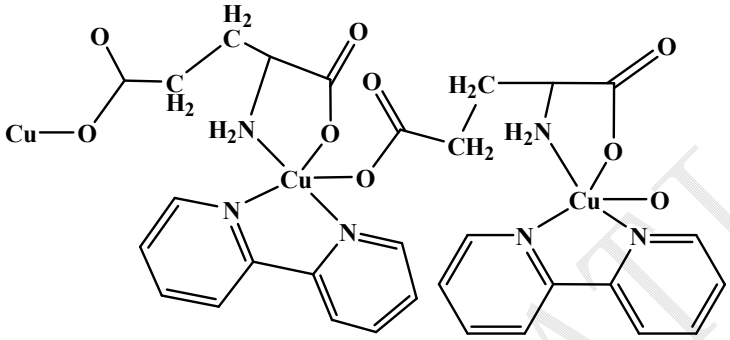

Figure 5

A new polynuclear copper(II) complex of singly deprotonated L-glutamic acid (L-glu), using 2,2′-bipyridine was synthesized in acidic pH (ca. 2.5) and characterized structurally[13]. In this complex, L-glutamic acid acts as a bidentate chelating ligand, leaving the protonated carboxylic acid free. Here two different type of species, 1. monomeric $[Cu(bipy)_2](BF_4)_2$ and 2.polynuclear $[Cu(bipy)(L\text{-}glu)H_2O]BF_4$ coexist in the solid state (figure 6). Another interesting structural aspect is thatthe polynuclear $[Cu(bipy)(L\text{-}glu)]_2]_n^{n+}$ units are joined together by syn-anti carboxylate bridges to form an enantiopure (M) helical chain and the $[Cu(bipy)_2]^{2+}$ represent a very rare example of the four-coordinate distorted tetrahedral geometry of Cu(II) in that species (figure 6).

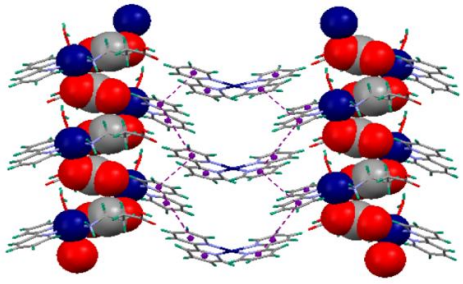

Figure 6

Another co-crystalline complex was also reported in this paper[13], where 1,10-phenanthroline was used as a co ligand, resulting a 1D polymeric chain of $[Cu(bipy)(L\text{-}glu)(ClO_4)]_n$ units joined together by weakly coordinating perchlorate ions and $[Cu(bipy)(L\text{-}glu)H_2O]^+$ units remains as mononuclear species between two 1-D polynuclear chains (figure 7).

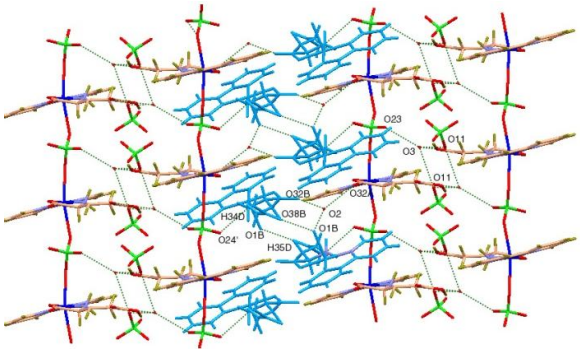

Figure 7

A new mononuclear copper(II) complex of singly deprotonated L-glutamic acid (L-glu), using 1,10-phenantroline was synthesized[13] in acidic pH and characterized structurally. The structure of the molecule consists of two independent monomeric $[Cu(phen)L(H_2O)]^+$ cations, two nitrate anions and four water molecules. The copper atom occupies a five-coordinate square pyramidal environment with a water molecule in the axial position (figure 8).

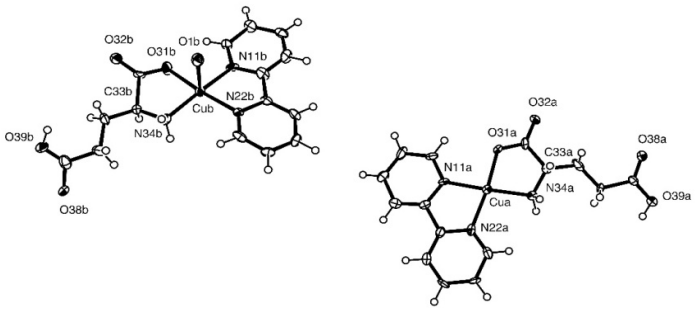

Figure 8

CONCLUSION

This paper emphasize on the versatile bridging modes of aspartic acid and glutamic acid to produce different types of polynuclear copper(II) complexes with interesting structure and magnetic properties. Aspartic acid shows only tridentate bi-negetive polydentate bridging modebut glutamic acid acts both as tridentate bi-negetive polydentate ligand and bidentate mono-negetive chetaling ligand.

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